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Research and development

Progress Report No. 25

Development of
Ultra Refractory Materials

RESEARCH CONTRACT NOrd-17175
May 1, 1961 through July 31, 1961

By: Peter T. B. Shaffer

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Bureau of Naval Weapons
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Washington 25, D. C.

August 16, 1961

SUMMARY

The research during the report period was a continuation of the study of the carbide system, ZrC-TaC. A study of spectral emissivity showed an apparent, reversible crystalline change in both ZrC and TaC but not in the solid solutions. Melting studies on the series are inconclusive due possibly to analytical discrepancies.

A preliminary study of materials for use in radomes has been initiated with its goal, the development of a radome material, more shock resistant than those presently available.

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FIGURES

I. INTRODUCTION

This is the twenty-fifth progress report on research sponsored by the Department of the Navy, Bureau of Naval Weapons, under Contract NOrd-17175. It covers the period 1 May 1961 through 31 July 1961.

The study of solid solutions of tantalum carbide and zirconium carbide was continued. The melting temperatures and calculated spectral emissivities showed a reversible change to occur on heating the pure carbides. This change is accompanied by a marked decrease in emissivity and resistivity. The measured melting temperatures are lower than the reported values. The cause of the low melting temperatures, due possibly to non-stoichiometry or failure to correct completely for emissivity, has not been resolved.

A survey has been started to determine whether radome materials with improved thermal shock resistance can be developed. A few "zero" expansion and low expansion ceramic bodies have been prepared for testing.

II. WORK PROGRESS

A. ZrC-TaC System

1. Melting Studies

The melting temperatures of a range of compositions have been measured. The melting temperatures are uniformly low, though quite reproducible not only within a particular hot-pressed sample of material but from one lot to another. Analyses are erratic due presumably to coprecipitation problems. The measured melting temperatures are listed in Table No. I without additional comment, pending a further study of the analytical procedures, stoichiometry, etc.

2. Emissivity Studies

During the direct-resistance heating of zirconium carbide bars, a marked change was noted at temperatures in excess of 3810°F. (2100°C.). Without a change in the applied voltages, a rapid increase in temperature, as much as 900°F. (500°C.), was noted. A reaction zone could be observed to spread along the length of the bar, followed by the previously mentioned apparent temperature increase.

In order to study this reaction in more detail a number of bars of zirconium carbide (1/8 x 1/8 x 3 inches) were prepared. In each

TABLE NO. I

Melting Temperatures
of
ZrC-TaC Compositions

<u>Composition</u>	Number of Samples	<u>Melting Temperature</u>			
		<u>Average</u>		<u>Deviation</u>	
		<u>°F.</u>	<u>°C.</u>	<u>°F.</u>	<u>°C.</u>
ZrC	8	5900	3260	45	25
7ZrC-TaC	8	6060	3350	45	25
4ZrC-TaC	5	6010	3320	115	65
3ZrC-TaC	5	6090	3365	45	25
2ZrC-TaC	4	6240	3450	25	15
ZrC-TaC	4	6340	3505	0	0
2TaC-ZrC	3	6430	3555	10	5
3TaC-ZrC	2	6520	3600	0	0
7TaC-ZrC	4	6320	3490	0	0
TaC	4	6400	3540	25	15

a hole (1/64 inch in diameter x 3/32 inch deep) was ultrasonically drilled near the middle. This hole provided "near blackbody" conditions for temperature measurement.

By measuring surface temperatures on areas polished with 400 grit diamond wheels and the internal or blackbody temperature, it was possible to calculate an approximate value for spectral emissivity. All temperatures were measured by means of a Leeds and Northrup optical pyrometer at a wave length of approximately 0.65 microns.

Subsequent experiment showed that not only is there a marked change in emissivity but that the actual temperature of the bar increases, accompanied by a decrease in resistivity of the sample bar.

Numerous zirconium carbide bars were examined during both heating and cooling cycles. The results of these observations show that at 4000°F. (2200°C.) a change in the nature of the zirconium carbide bar occurs accompanied by a decrease in spectral emissivity and a decrease in resistivity. The change is reversible, with both resistivity and emissivity returning to their original values. The transformation shows a hysteresis effect of nearly 900°F. (500°C.) which is apparently not time dependent (Figure 2).

An additional observation is that the bars on heating through the range of 3630-4530°F. (2000-2500°C.) frequently split lengthwise, presumably due to an increase in volume accompanying the transformation (Figure 1). This volume increase will be studied later by means of a direct reading dilatometer in which the change in length of the specimen is measured directly by means of long focal length microscopes.

A similar, though less sharply defined, change has been observed with tantalum carbide, but not with any of the solid solution compositions in the tantalum carbide-zirconium carbide series (Figures 3 through 10). Since these observations were made, a report describing similar observations made by General Electric on tantalum carbide has been released⁽¹⁾.

(1) "Carbonization of Plastics and Refractory Materials Research,"
A. A. Watts, G. M. Kibler, T. R. Riethof and J. A. Coffman,
WADD-TR-60-646, Part I, February, 1961.

B. Radome Materials

The research on radome materials is directed specifically to the development of more thermal shock resistant radomes. The work, still in its very early stages, is divided into two areas. The first is a study of presently available materials with the object of finding means to increase their thermal shock resistance. The second is a study of low and "zero" expansion compositions whose thermal shock resistance is excellent, to find those with acceptable electrical properties.

The work on the first phase has been confined to obtaining samples of available materials for testing. An impartial measurement of the physical, mechanical and electrical properties of these materials, under identical conditions, will permit a realistic evaluation from which future experiments may be planned.

Phase two has been directed specifically toward the preparation of low expansion compositions using high purity reactants. The low expansion area of the $\text{Al}_2\text{O}_3\text{-Li}_2\text{O-SiO}_2$ ternary system will be evaluated, not on the usual basis of thermal expansion but on electrical properties. Several compositions have been prepared; however, test data are not available as yet.

III. FUTURE WORK

Future work will be directed toward determining the cause of the consistently low measured temperatures in the carbide studies and to a thermal expansion study of the high temperature phase change in zirconium and tantalum carbides.

The work on radome materials will be accelerated as materials become available. Thermal shock testing and physical property measurements on presently available radome materials will be the first experimental program. Synthesis and evaluation of low expansion compositions of high purity will be undertaken.



Figure 1 - Zirconium Carbide Melting Point Samples.
a. Before heating
b. Heated through inversion, note splitting

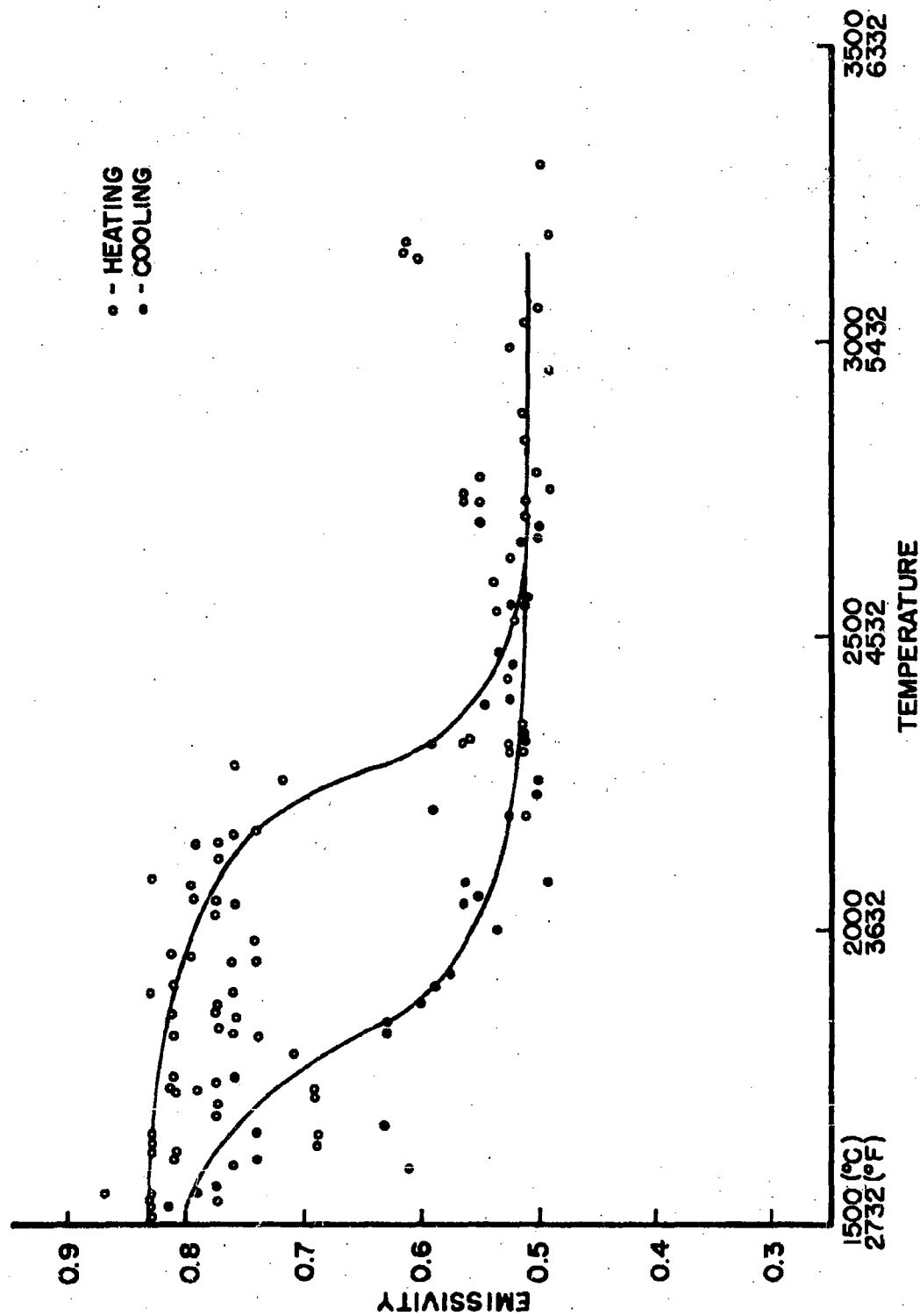


FIGURE 2.
SPECTRAL EMISSIVITY OF
ZrC AT 0.65 μ

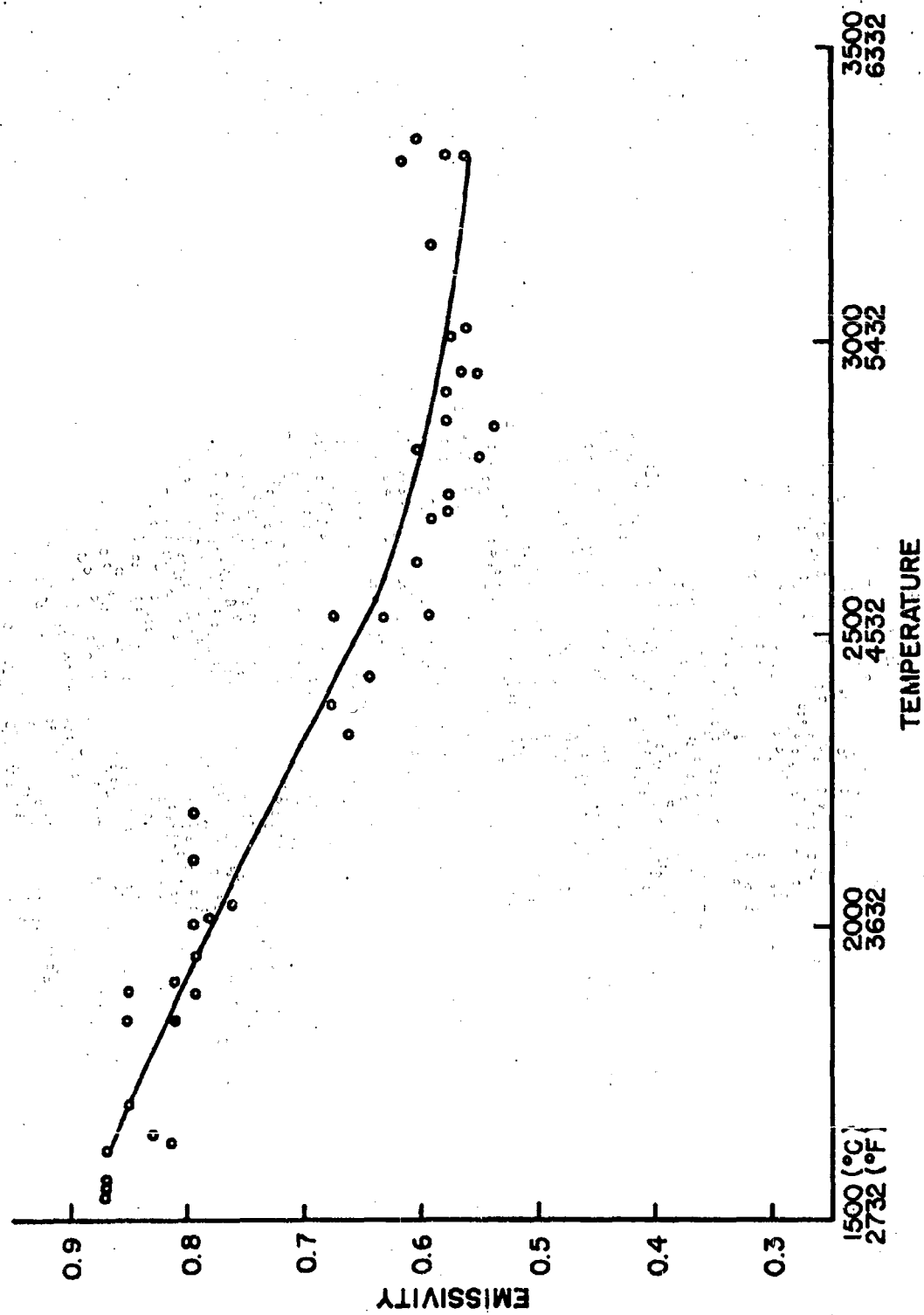


FIGURE 3.
SPECTRAL EMISSIVITY OF
7ZrC-TiC AT 0.65 μ

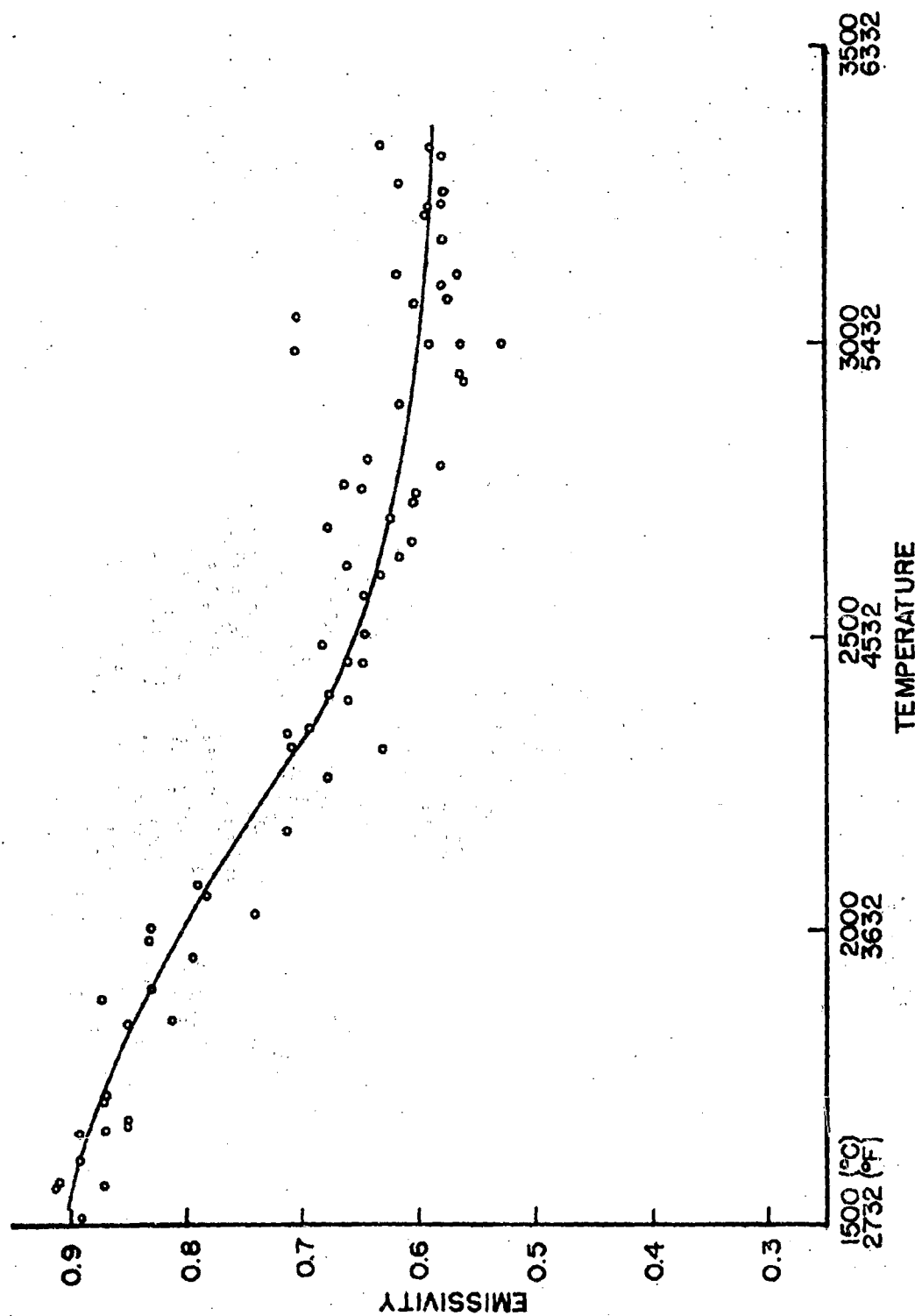


FIGURE 4.
SPECTRAL EMISSIVITY OF
4ZrC-TbC AT 0.65 μ

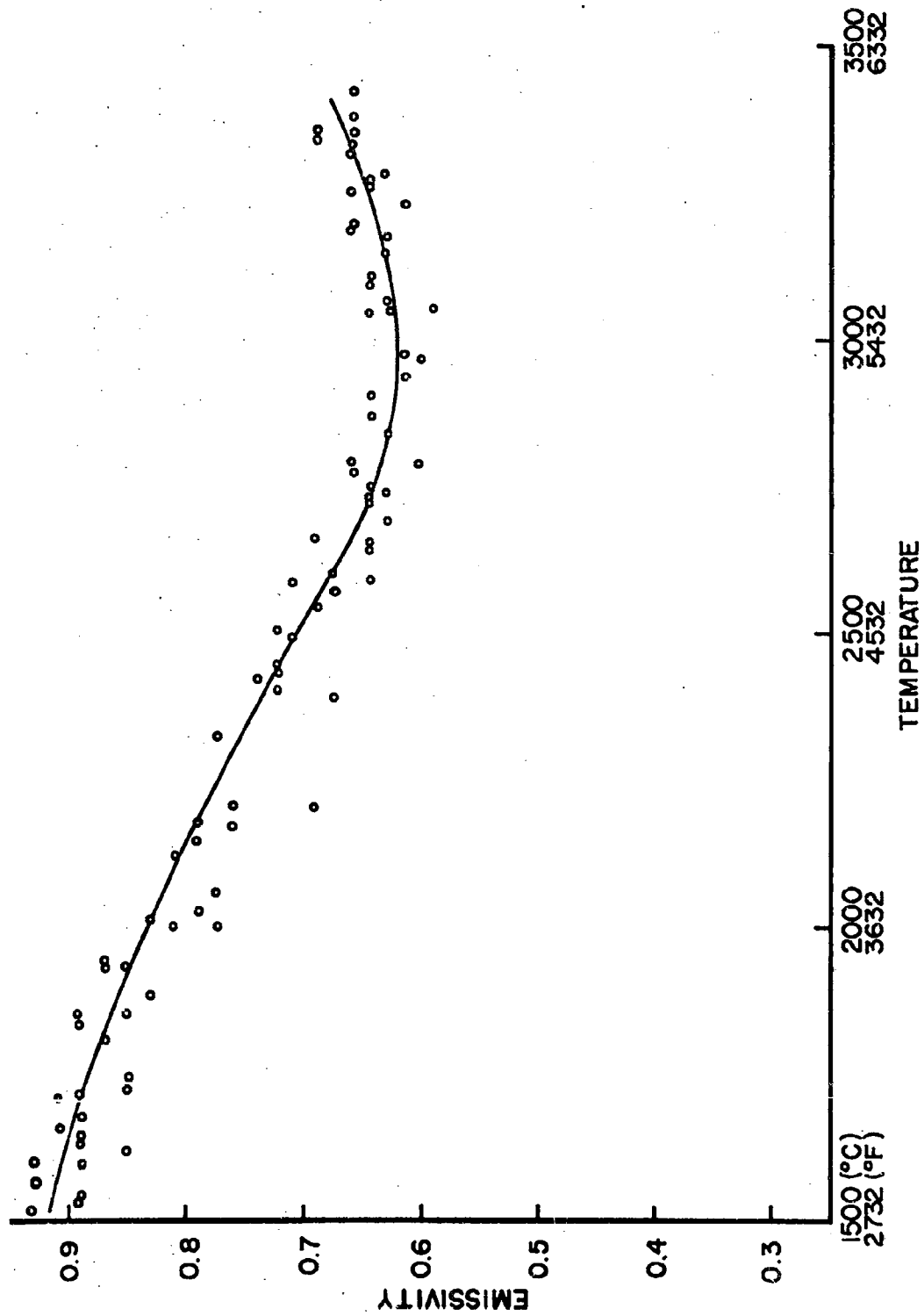


FIGURE 5.
SPECTRAL EMISSIVITY OF
3ZrC-TaC AT 0.65 μ

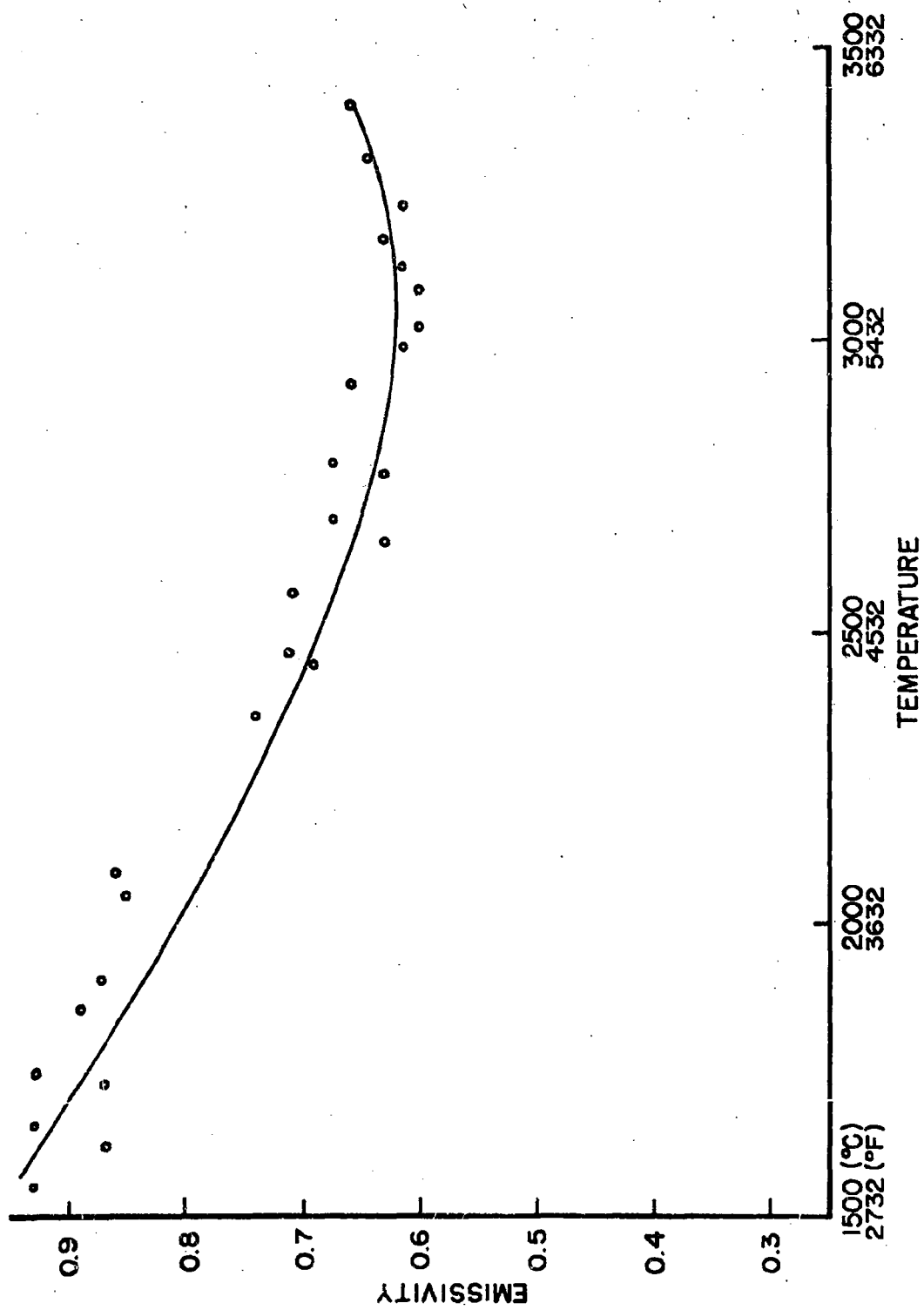


FIGURE 6.
SPECTRAL EMISSIVITY OF
TaC - ZrC AT 0.65 μ

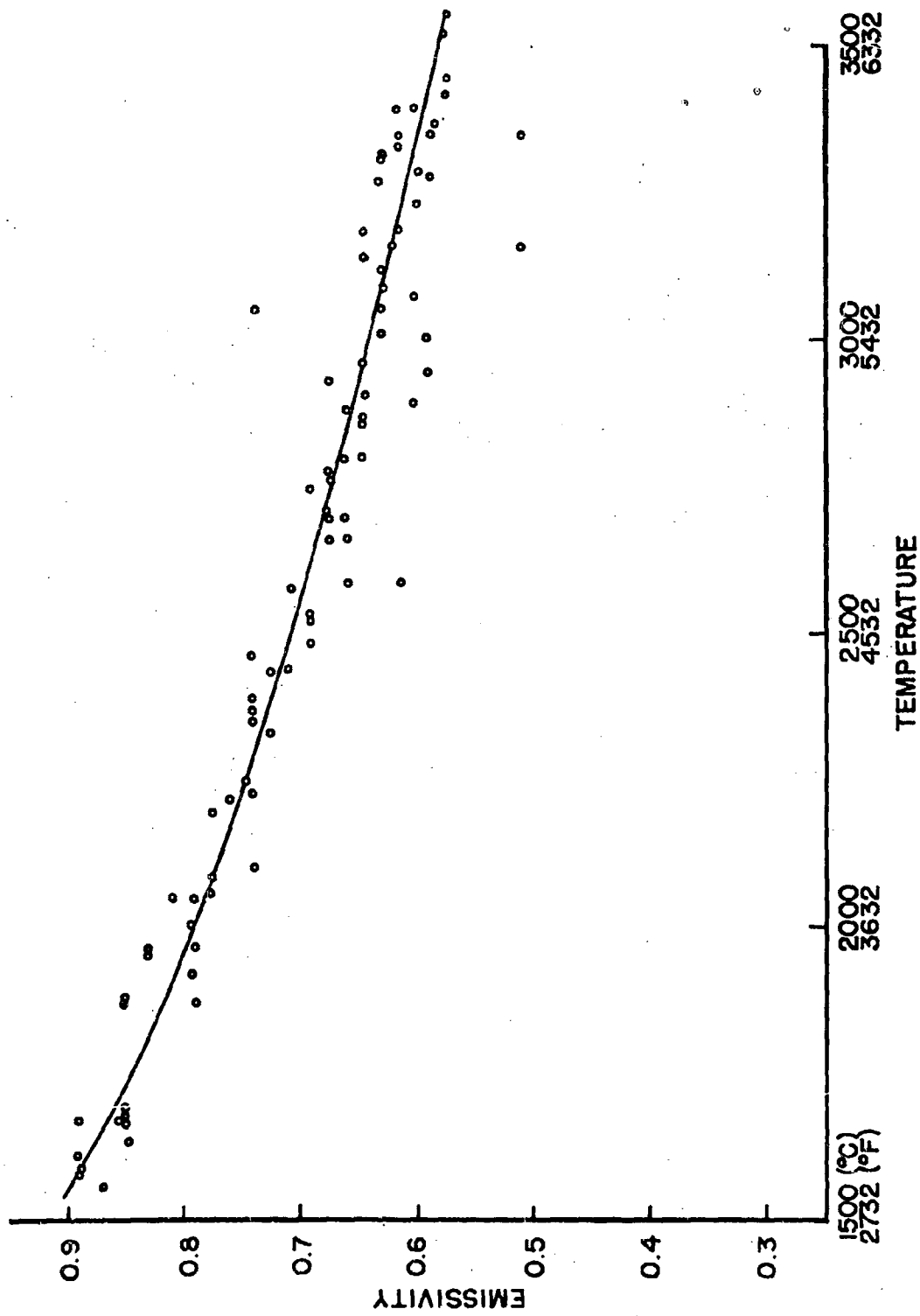


FIGURE 7.
SPECTRAL EMISSIVITY OF
2 TaC - ZrC AT 0.65 μ

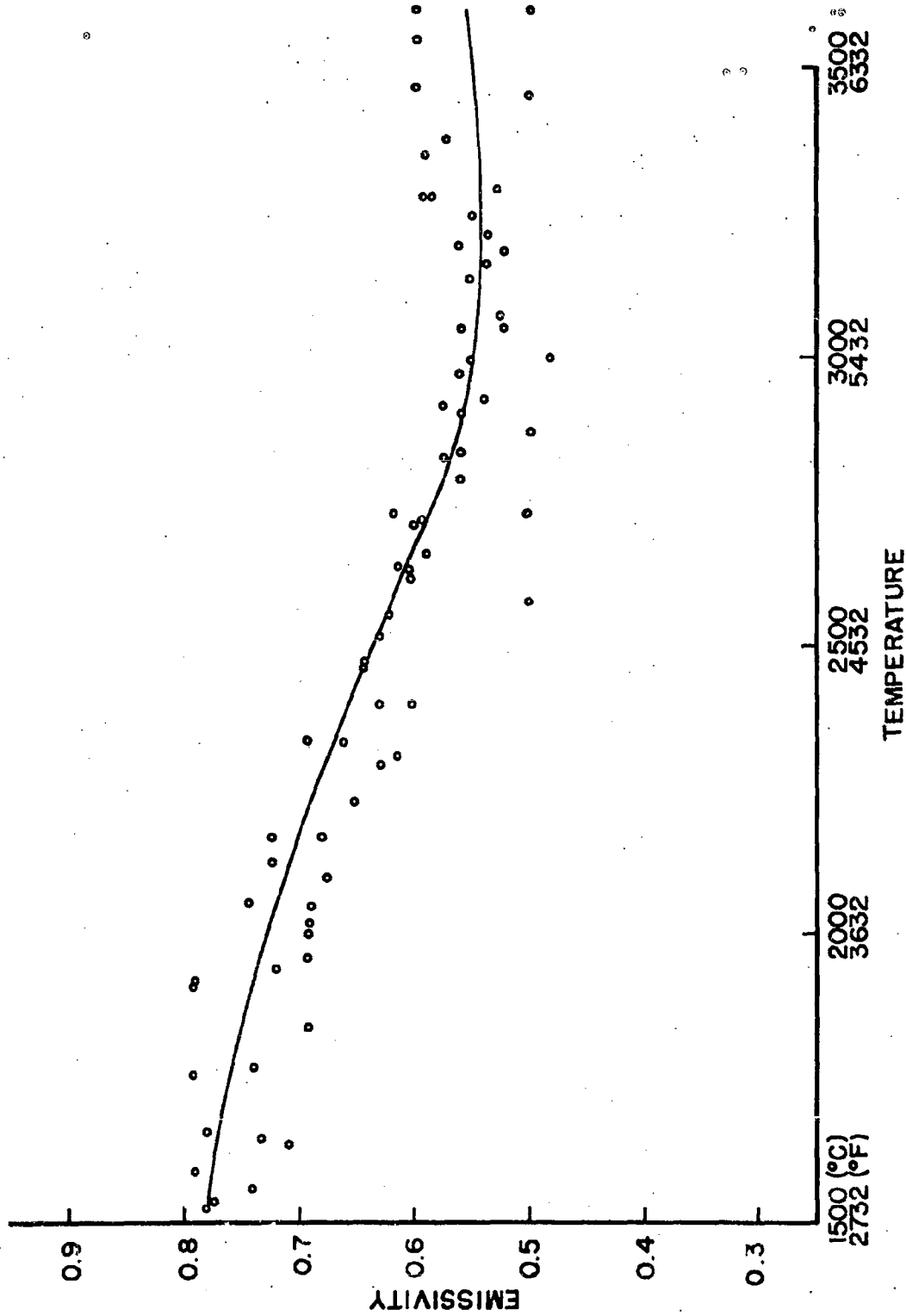


FIGURE 8.
SPECTRAL EMISSIVITY OF
3TaC-ZrC AT 0.65 μ

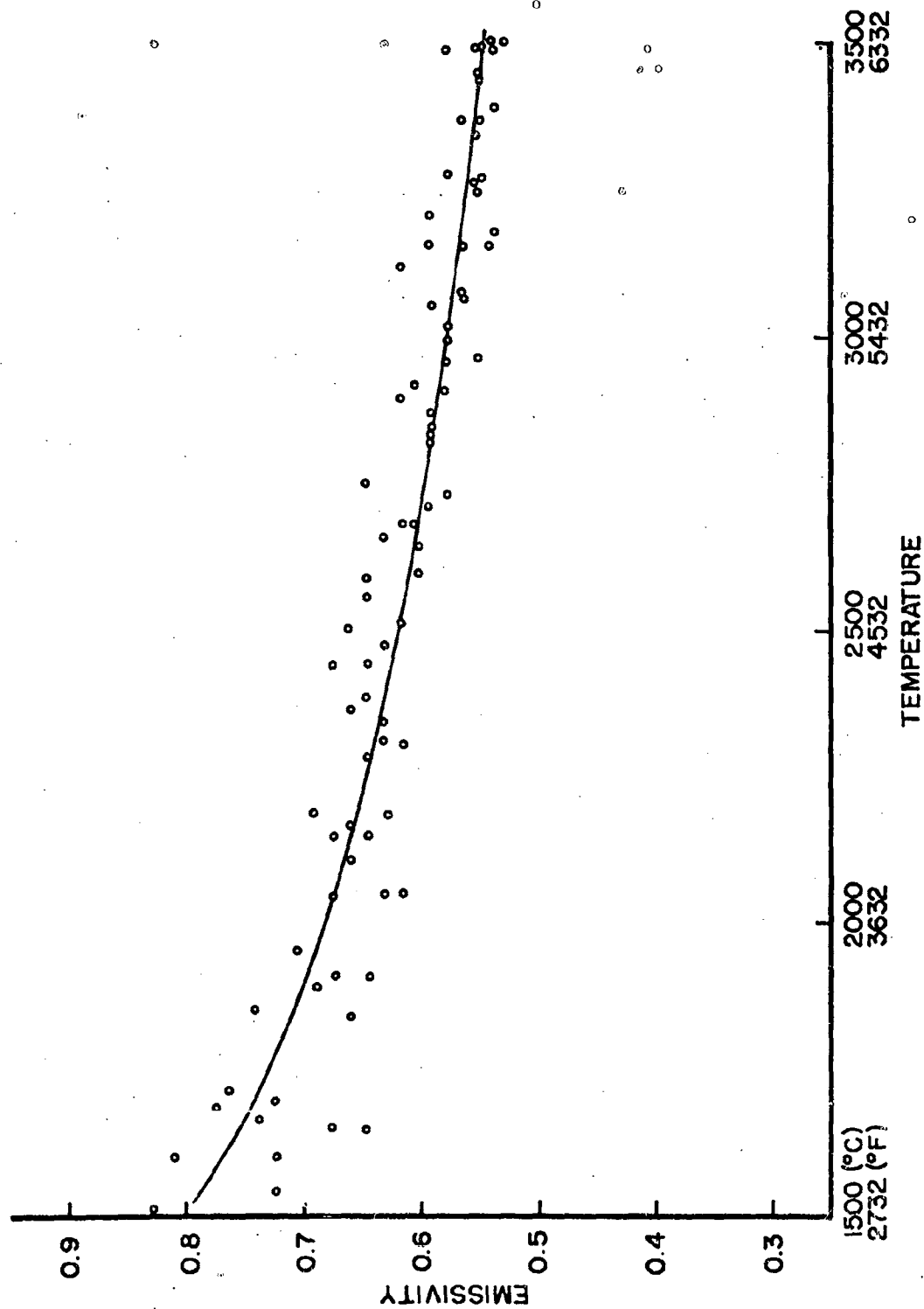


FIGURE 9.
SPECTRAL EMISSIVITY OF
7 TaC-ZrC AT 0.65 μ

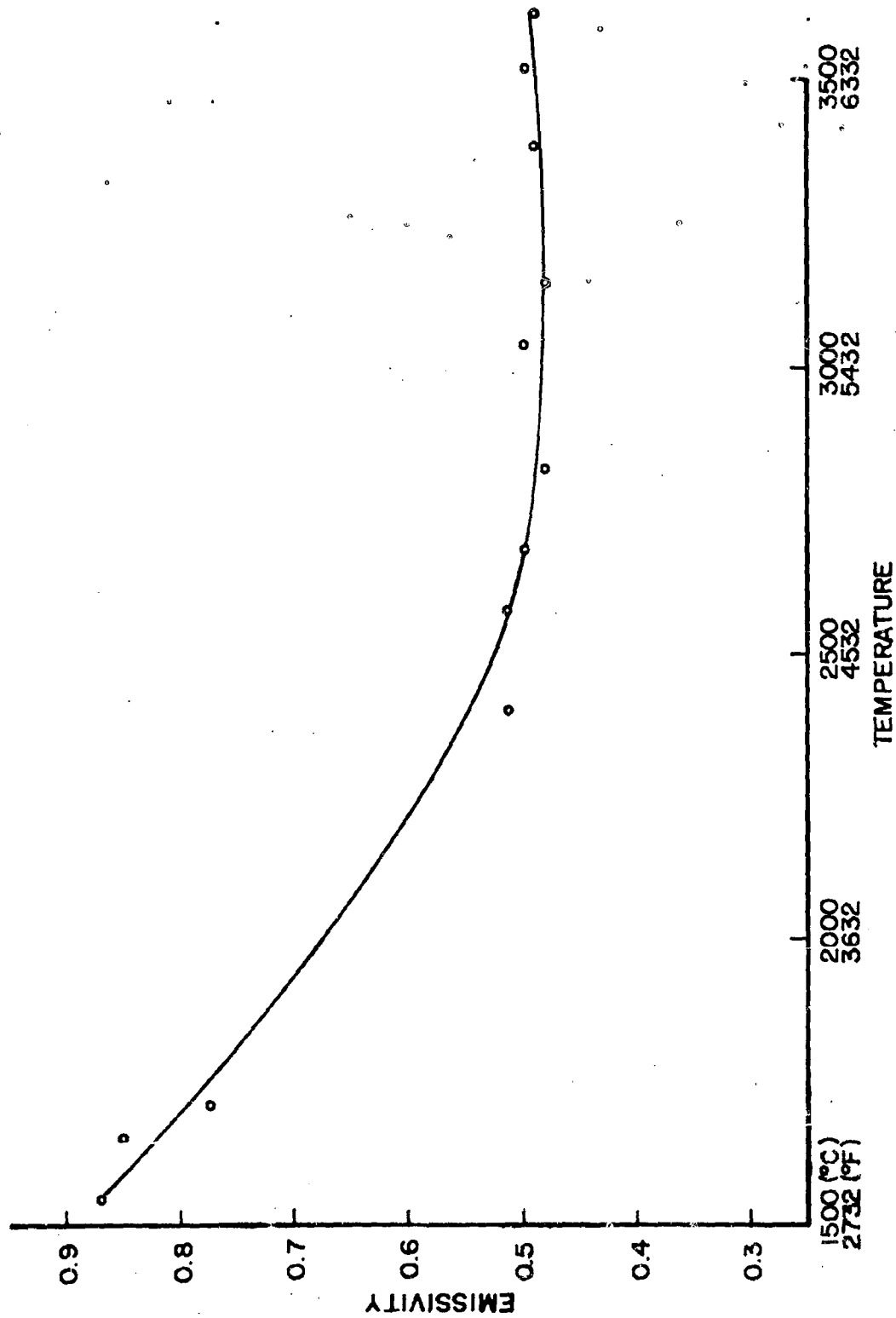


FIGURE 10.
SPECTRAL EMISSIVITY OF
TcC AT 0.65 μ

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